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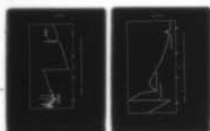
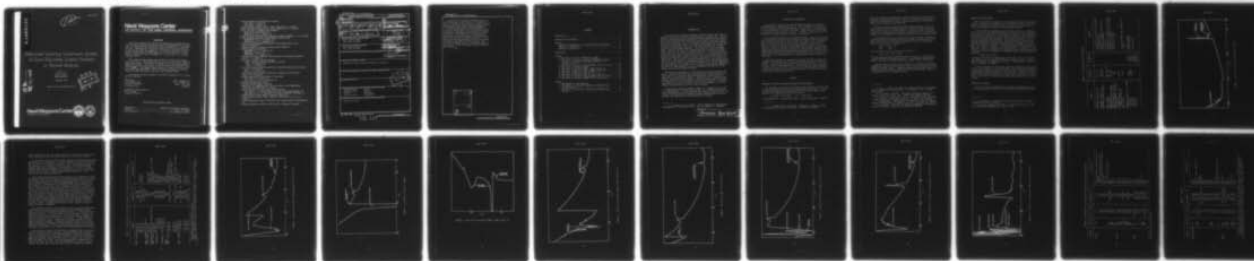
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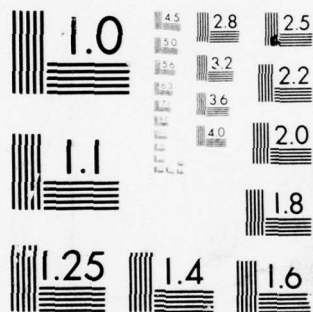
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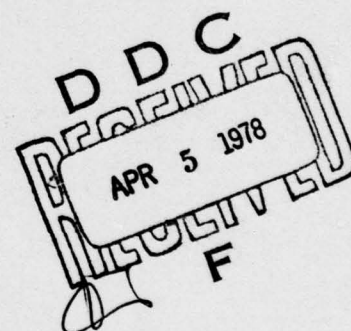
Differential Scanning Calorimetry Studies of Some Electrolyte Systems Pertinent to Thermal Batteries

by
Dwight A. Fine
Aaron N. Fletcher
Research Department

FEBRUARY 1978

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FOREWORD

This report presents the results of differential scanning calorimetry studies carried out during the period from November 1976 to August 1977, in connection with the thermal battery program of the Chemistry Division. Representative traces are shown and the principal features of the various scans are summarized. A portion of this work was summarized in NWC Technical Memorandum 3334, *The Calcium Anode in Molten Nitrate Electrolytes*, by M. H. Miles, D. A. Fine, and A. N. Fletcher (November 1977).

The thermal battery program was supported by three tasks during Fiscal Year 1977. Passivating films at the calcium anode was supported under Task ZR01305. The thermal decomposition of electrolyte/oxidizer mixtures in contact with anodic or cathodic metals was supported under Task ZF6112001. The electrochemical nature of single cells was evaluated under Task ZF54595003. This differential scanning calorimetry work falls under the area of the first two indicated tasks.

This report has been reviewed for technical accuracy by A. H. Lepie and M. H. Ritchie.

Approved by
E. B. ROYCE, *Head*
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9 February 1978

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(U) The thermal behavior of some electrolyte systems which are potentially useful in thermal batteries has been investigated by differential scanning calorimetry. The reactivity of calcium metal in molten nitrates and thiocyanates has been studied. The nitrate systems are the most promising. It has been found that a passivating layer of calcium oxide is formed on the metal in molten nitrates; this layer can be broken down in a controllable manner by the addition of Lux-Flood acids or alkali halides to the nitrates.

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INTRODUCTION

The differential scanning calorimetry studies reported here were carried out in connection with the thermal battery program at NWC. Thermal batteries employ solid electrolytes which become conducting upon melting. The battery is activated by ignition of a pyrotechnic heat source which melts the electrolyte. Most of the thermal batteries presently employed in missile systems make use of a lithium chloride-potassium chloride mixture as the electrolyte, calcium as the anodic material, and calcium chromate as the oxidizing material. This system has several disadvantages. Calcium can react with lithium chloride to form molten lithium metal, which in turn forms a calcium-lithium alloy. This alloy causes electrical noise and can short-circuit the cell. Potassium chloride and calcium chloride form an insoluble double salt which precipitates on the anode; this precipitate limits the useful temperature of the battery to above 490°C. The relatively high melting point of the electrolyte limits activation of the battery to temperatures above 350°C, and decomposition of the oxidizer places an upper limit of 600°C on the internal temperature. For these reasons, and because of the increasing power density demands of new missiles, investigation of new electrochemical systems for use in thermal batteries was deemed advisable.

Nitrates and thiocyanates are particularly attractive materials for study. Alkali thiocyanates are low melting, form low-melting eutectics with other salts, and have shown good performance characteristics in laboratory electrochemical studies.¹ Nitrates are also relatively low melting, and possess a high degree of oxidizing power, thereby offering the possibility of the electrolyte serving as the oxidizer. An oxidizing electrolyte requires an anode that is electrochemically active but chemically passivated, in order to avoid corrosion.

Differential scanning calorimetry (DSC) is a valuable tool for initial investigations of electrolyte systems, as it provides information on melting behavior, thermal stability, and chemical reactivity. It can also provide information on possible hazards connected with oxidizing systems, and requires only small quantities of material.

¹ R. E. Panzer and M. J. Schaer. "Electrochemistry in Fused Alkali Thiocyanates," *J. Electrochem. Soc.*, Vol. 112 (1965), pp. 1136-1143.

EQUIPMENT AND TECHNIQUES

The instrument employed for the differential scanning calorimetry measurements was a Perkin Elmer DSC-1b. This instrument permits detection of exotherms and endotherms between 0°C and 500°C. A scanning rate of 10°/min was used for most of the runs. Thermal behavior was recorded on a Honeywell Electronik 194 strip chart recorder. The DSC-1b was calibrated with standard samples of indium, tin and lead.

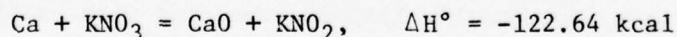
Runs involving calcium metal presented problems. Exposure of calcium to the atmosphere produced a thick grayish coating of oxide or hydroxide. When stored in a dry box to avoid contact with oxygen, the metal developed a brownish film due to reaction with nitrogen to form calcium nitride. For these reasons, calcium samples were scraped with a razor blade just prior to the runs in which they were employed, and argon gas rather than nitrogen was used to purge the sample holder assembly. Most samples were run in sealed aluminum pans; open pans were used when visual observation was desired. Because of the hygroscopicity of some of the salts used in the investigation, most samples were prepared and sealed in a dry box.

Qualitative analysis of residues for nitrate and nitrite was accomplished by removing the pan cover, dissolving the residue in about 5 ml of water, and measuring the ultraviolet absorption spectrum of the solution on a Cary 14 spectrophotometer. Nitrate shows an absorption peak at 300 nm, nitrite at 355 nm. The presence of nitrite can be confirmed by running the spectrum of an acidified solution, as HNO_2 shows a multi-peaked band centered around 365 nm.

RESULTS

BEHAVIOR OF CALCIUM IN MOLTEN NITRATES AND THIOCYANATES

No exothermic reactions of calcium with molten nitrates, thiocyanates or nitrate-thiocyanate mixtures were detected by the DSC runs. This indicates the formation of a protective film, most likely oxide, on the calcium; this film prevents reactions such as



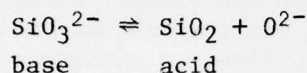
from proceeding to a significant extent. Brough and Kerridge² observed

² B. J. Brough and D. H. Kerridge. "Reactions of Metals in Fused Nitrate Eutectic," *Inorg. Chem.*, Vol. 4 (1965), pp. 1353-1356.

reactions (sometimes violent) when calcium turnings were added to molten potassium nitrate-lithium nitrate eutectic; in their work, the molten nitrate was evacuated and stirred. The stirring process could serve to break down the oxide layer mechanically.

In order to achieve a working battery system, chemical control of the protective film is needed, so that the film will protect the anode from corrosion but can be broken down to a sufficient extent to permit reaction of calcium with the oxidizer. One possible way to achieve this control is by the addition of Lux-Flood acids to the electrolyte material.

The Lux-Flood concept of acid-base reactions describes acid-base behavior in terms of the oxide ion³⁻⁵ and is useful in dealing with inorganic melt reactions. Lux and Flood define a base as an oxide donor, and an acid as an oxide acceptor, e.g.,



In the present study, the reaction of interest is



An acidic species with a suitable affinity for oxide ion would be able to break down the passivating CaO layer. Possibilities among species known to be acidic in melts include PO_3^- , $\text{Cr}_2\text{O}_7^{2-}$, B_2O_3 , Ag^+ and Li^+ .

Another possibility would be the addition of ions such as chloride, bromide and iodide, which are known to exert local activation effects on passivating oxide films.^{6,7} Numerous runs were made on nitrates or thiocyanates to which Lux-Flood acids or halides had been added. Results are presented in the following sections.

³ H. Lux. "'Acids' and 'Bases' in a Fused Salt Bath: the Determination of Oxygen-ion Concentration," *Z. Elektrochem.*, Vol. 45 (1939), pp. 303-309.

⁴ H. Flood and T. Forland. "The Acidic and Basic Properties of Oxides," *Acta Chem. Scand.*, Vol. 1 (1947), pp. 592-604, 781-789.

⁵ H. Flood, T. Forland and B. Roald. "Relative Acid-Base Strengths of Some Polyacids," *Acta Chem. Scand.*, Vol. 1 (1947), pp. 790-798.

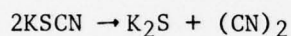
⁶ J. Augustynski. "Breakdown of the Passivity of Certain Electrochemically Active Metals," *Corrosion Sci.*, Vol. 13 (1973), pp. 955-965.

⁷ H. J. Engell. "Stability and Breakdown Phenomena of Passivating Films," *Electrochim. Acta*, Vol. 22 (1977), pp. 987-993.

BEHAVIOR OF THIOCYANATES

DSC runs were made on mixtures of potassium thiocyanate and potassium nitrate. The mixture containing 40 mol % thiocyanate and 60 mol % nitrate was selected for further study, as it showed a low melting point (131°) while having a relatively low thiocyanate content.

Calcium showed no exothermic reaction with the mixture. Addition of B_2O_3 (12 wt %) to the mixture produced no exotherms. A large exotherm was produced by addition of ≥ 20 wt % $NaPO_3$. Several runs were made with oxidizers in the absence of calcium and in open sample pans; decomposition of thiocyanate was indicated. $CaCrO_4$ showed reduction to Cr(III), and V_2O_5 showed reduction to V(IV). This reduction of V_2O_5 has been observed previously;⁸ the reduction product is predominantly VO_2 , and numerous decomposition products of thiocyanate are formed, among them SO_4^{2-} , CN^- , NO_3^- , S, and O_2^{2-} . $CuSCN$ showed vigorous decomposition in KNO_3 , and evidence of formation of cuprous sulfide. A mixture of 13 mol % $Cd(NO_3)_2$ with the 40/60 mol % thiocyanate/nitrate showed decomposition starting at 340°, with formation of cadmium sulfide. The decomposition reaction



is known to take place at temperatures above 250°.⁸ This would explain the formation of the insoluble cadmium and cuprous sulfides. Results with thiocyanates are summarized in Table 1. Representative traces are shown in Figures 1 through 3.

It was concluded that thiocyanate exhibited undesirable chemical behavior in the presence of useful oxidizers. Also, thiocyanate presents toxicological hazards on account of the formation of cyanogen gas by the decomposition reaction noted above, and the risk of formation of highly toxic cyanide fumes when heated to decomposition or upon contact with water or acid fumes.⁹ Further effort was concentrated solely on nitrate systems.

BEHAVIOR OF NITRATES

Most of the DSC work reported here was done with potassium nitrate, or a eutectic mixture (50/50 mol %) of potassium and sodium nitrates.

⁸ D. H. Kerridge. *Advances in Molten Salt Chemistry*. New York, Plenum Press, 1971, pp. 249-273.

⁹ N. I. Sax. *Dangerous Properties of Industrial Materials*. New York, Reinhold Publishing Corp., 1957, p. 1181.

TABLE 1. DSC Results for Thiocyanates.

Sample	Endotherms, °C	Exotherms, °C	Remarks
KSCN/ KNO_3 (40/60 mol %)	120, 131		Dec. > 400°. Selected as good KSCN/ KNO_3 mixture
KSCN/ KNO_3 (40/60) + Ca	120, 130		Dec. starts ~400°
KSCN/ KNO_3 (40/60) + CaCrO_4	122-130		Darkens at 300-360°; reduction to Cr(III) indicated
KSCN + CuSCN	130, 136, 176		Dec. > 250°
KNO_3 + CuSCN	130, 350		Vigorous dec. 370-390°; turns black
KSCN/ KNO_3 (40/60) + CuSCN	110, 130		Blackens at 300-380°; no dec. peaks
KSCN + $\text{Cd}(\text{NO}_3)_2$ (17 mol %)	130		Forms CdS at > 230°
KSCN/ KNO_3 (40/60) + $\text{Cd}(\text{NO}_3)_2$ (13 mol %)	130		Forms CdS at > 340°
KSCN/ KNO_3 (40/60) + Ca + B_2O_3 (12.7 wt %)	120, 330		
KSCN + V_2O_5	~180		Turns greenish-black; reduction to V(IV)
KSCN/ KNO_3 (40/60) + Ca + NaPO_3 (32 wt %)	~116	~350	Strong exotherm
(25 wt %)	115-120	335-370	Strong exotherm
(21 wt %)	~116	~350	Weak exotherm
(13 wt %)		320-360	
(8.5 wt %)		not well defined	

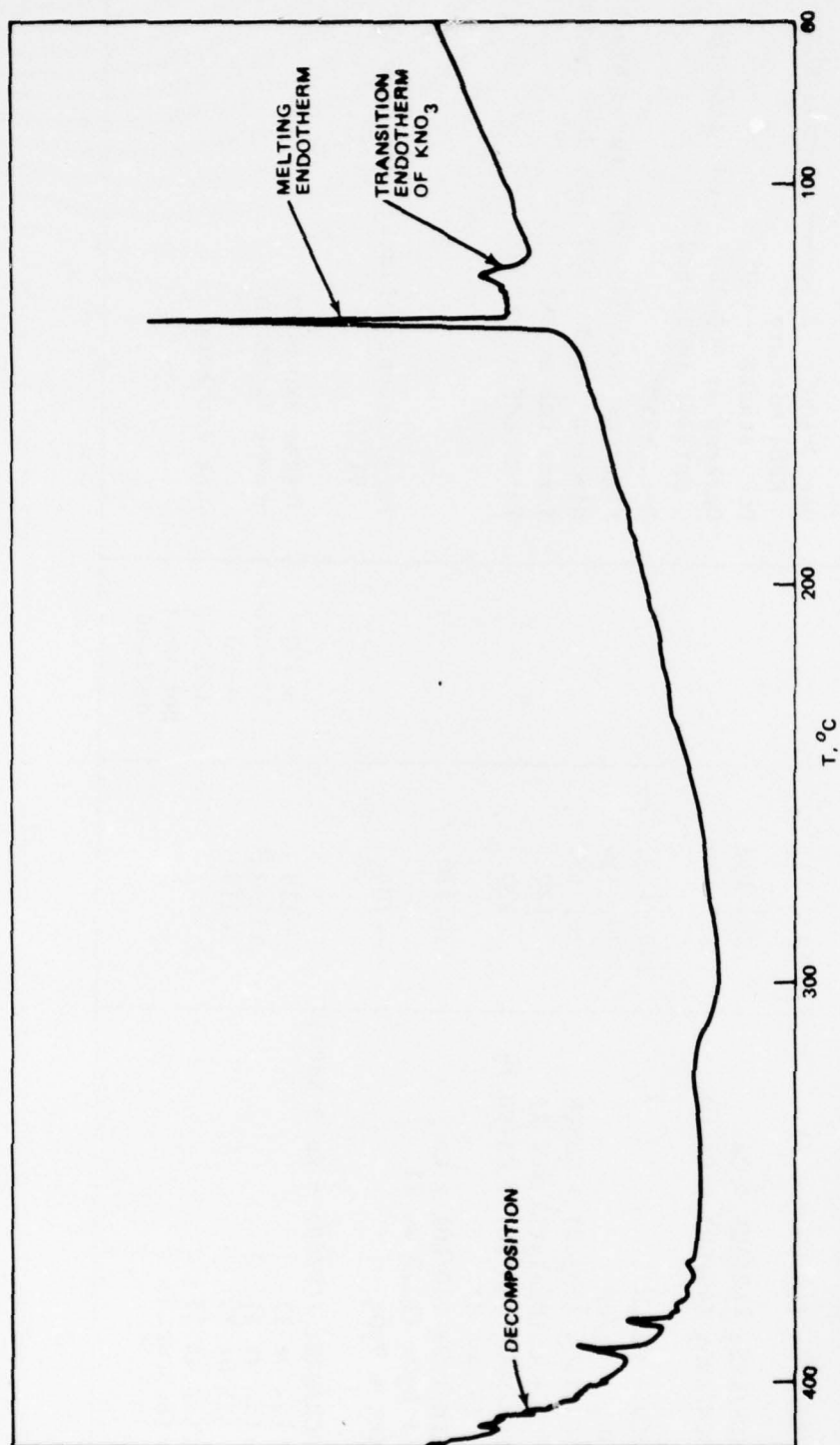


FIGURE 1. DSC Trace of 40 mol % KSCN/60 mol % KNO_3 .

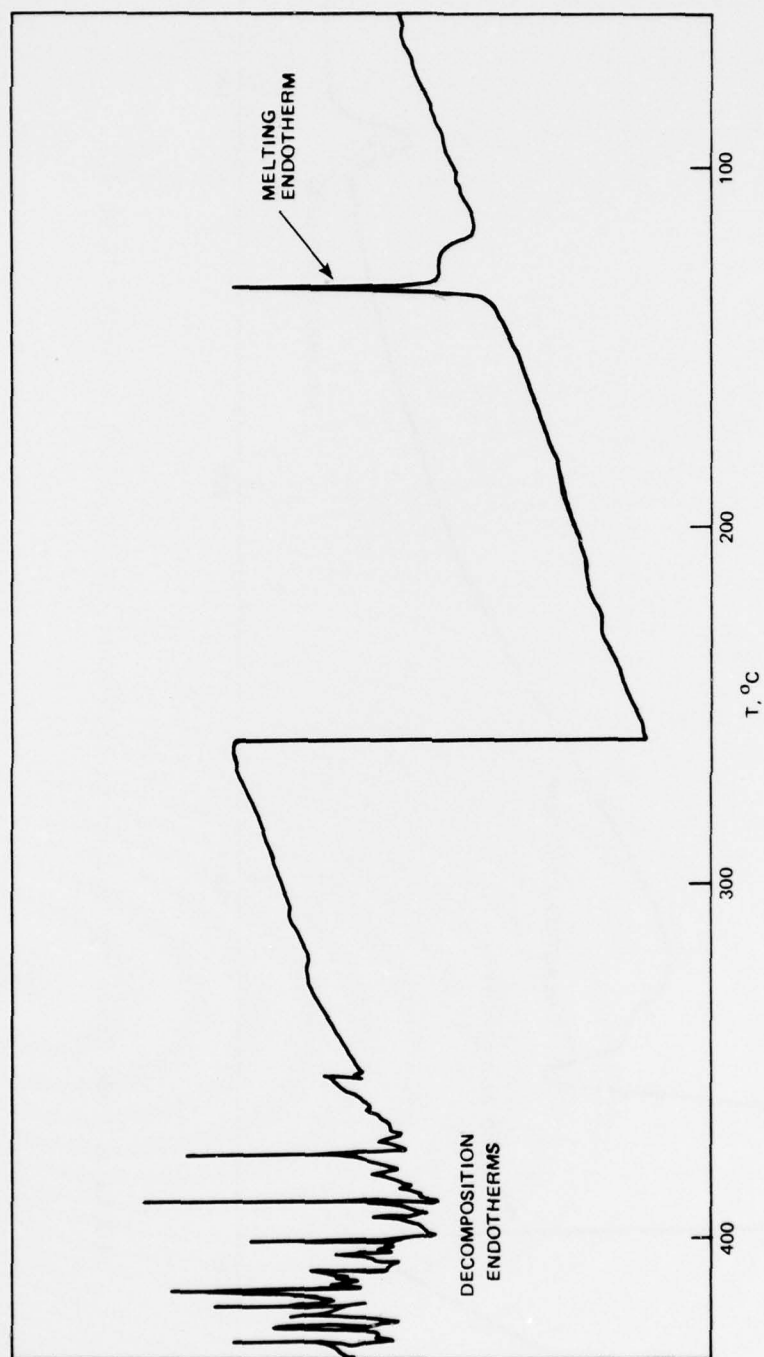


FIGURE 2. DSC Trace of Calcium in 40 mol % KSCN/60 mol % KNO_3 .

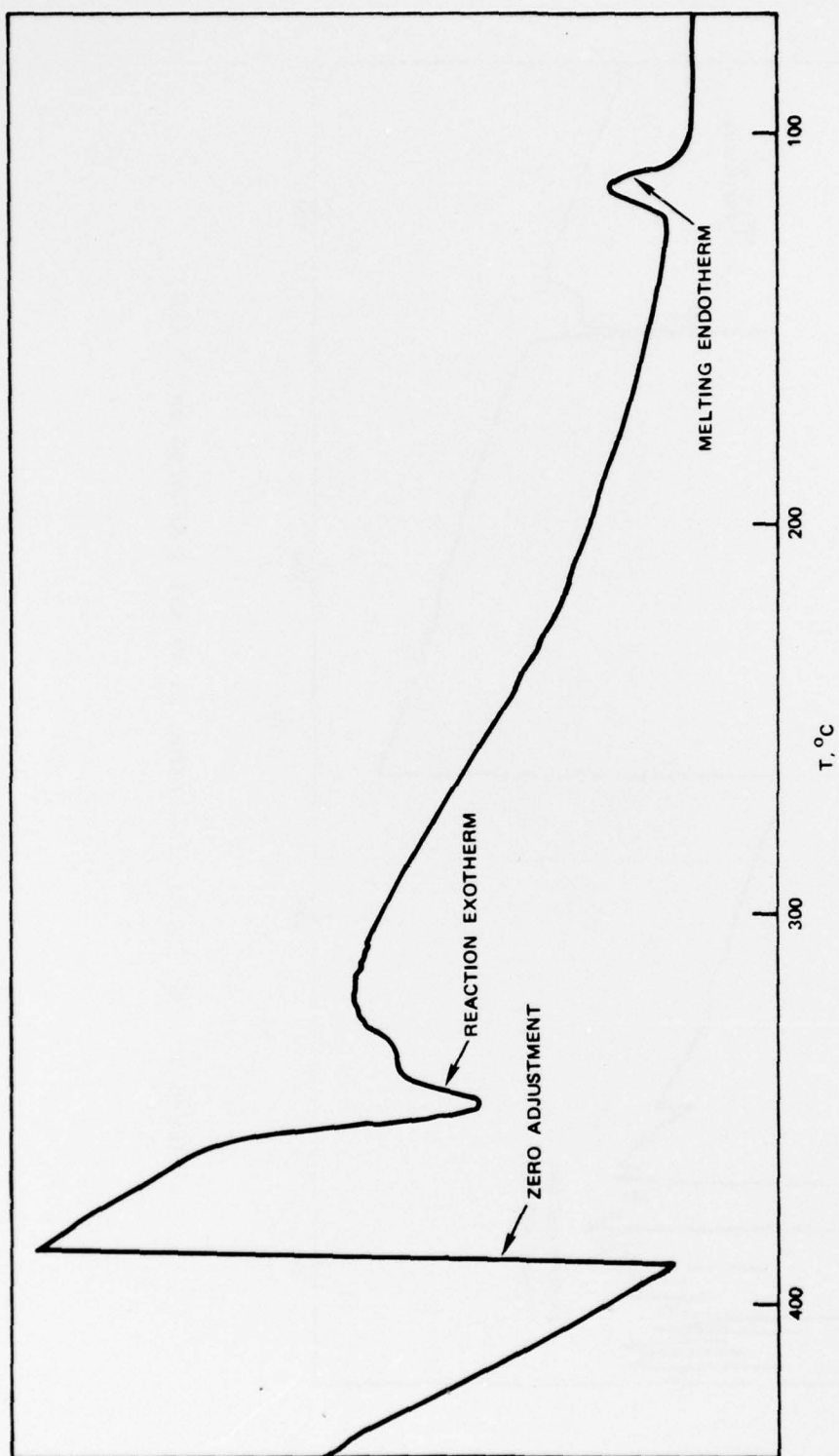


FIGURE 3. DSC Trace of Calcium in KSCN/KN0₃ (40/60 mol %) + NaPO₃ (32 wt %).

These nitrates are much less hygroscopic than lithium or rubidium nitrate, and potassium forms the most soluble oxide of all the alkali metals.

As mentioned previously, these nitrates showed no exothermic reactions when heated with calcium metal. Several Lux-Flood acids were tested with the nitrates in the presence of calcium. B_2O_3 gave inconsistent results, and appeared to be insoluble in molten nitrate. Sodium metaphosphate ($NaPO_3$) showed small exotherms at concentrations ca. 20 wt %. Another compound which yielded exotherms was cuprous chloride; less than 10 mol % of $CuCl$ was required to produce a deep exotherm starting ca. 350° . Cuprous oxide also showed an exotherm.

When calcium was heated with silver nitrate, a very sudden and vigorous reaction took place as soon as the nitrate melted. Mixtures of silver and potassium nitrates also showed exotherms when heated with calcium; the size and temperature of the exotherms depended on the proportion of silver nitrate. Examination of the residues from three different runs, where $AgNO_3$ was 100, 38 and 14 mol % showed the presence of metallic silver. The ultraviolet absorption spectra of neutral aqueous solutions of the soluble portions of the residues showed that most of the nitrogen was still in the form of nitrate, with very little reduction to nitrite. This indicates that the main reaction between calcium and silver nitrate involves reduction of silver ion rather than reduction of nitrate. Mixtures of potassium and cadmium nitrates were found to yield exotherms with calcium, although neither nitrate by itself showed such behavior. At least 10 mol % of cadmium nitrate was required. Results of all of the above studies are summarized in Table 2. Some typical traces are shown in Figures 4 through 7.

An extensive series of runs was made in which calcium was heated with alkali nitrates containing varying proportions of different halides. Some typical traces are shown in Figures 8 through 11. Results are summarized in Table 3. It is seen that in all of the alkali nitrates, at least two alkali halides will serve to promote reaction of nitrate with calcium, when halide concentration is ca. 10 mol %. Iodide appears to exert the strongest effect. Blank runs with either calcium or halide absent showed no exotherms. Ultraviolet absorption spectra were run on aqueous solutions of residues from representative runs in which strong exotherms were observed. In all cases, a high proportion of nitrite was indicated, whereas spectra of samples before heating showed only nitrate.

Several factors seem to be influential, including halide ion, cation, halide concentration and solubility. At approximately equal concentrations of potassium halide, the decreasing order of ability to promote reaction of nitrate with calcium is $KI \gtrsim KBr > KCl \sim KF$ in molten $LiNO_3$, $NaNO_3$ and $(Na/K)NO_3$, while the order is $KF \sim KI \gg KBr \sim KCl$ in molten KNO_3 and $RbNO_3$. The effect of halide concentration is apparent in the series with $LiNO_3$ and $LiCl$. $LiCl$ concentrations ≥ 11.0 mol % cause a violent reaction, and a flash of light is seen; concentrations between

TABLE 2. DSC Results for Calcium in Mixtures of Nitrates and Lux-Flood Acids.

Sample ^a	Endotherms, °C ^b	Exotherms, °C ^c
KN ₃ + B ₂ O ₃ (31.0 wt %) (24.0 wt %) (23.0 wt %) (10.2 wt %) (7.5 wt %)	120, 340 120, 340 120, 260, 337, 341 120, 340 120, 305, 340	341-360 w 375-440 w
KN ₃ + Ba(NO ₃) ₂ (12.5 mol %) KN ₃ + NaPO ₃ (23 wt %) (21 wt %)	294-300 ~318 ~312 ~220	~310, 320 w 305, ~321 w ~284, 340 w, dec. 375-400 320-400, >440 Dec. >410
(Na,K)NO ₃ (50/50 mol %) + NaPO ₃ (19 wt %) KN ₃ + CuCl (7.2 mol %) (3.7 mol %)	114, 300 120, 223 120, 220 120, 220 120, 230 120, 230	355-385 s 370-400 m 340-390 ~428 s ~430 w
(Na,K)NO ₃ + CuCl (6.7 mol %) (5.1 mol %) (2.3 mol %)	~160 ~120 3 between 115 & 136	203-218 vs 129-138, 180-210 s, ^m 220-238, 241-247, 252-257 m (general dec. >200)
(Na,K)NO ₃ + Cu ₂ O (9.6 mol %) (3.0 mol %)	120, 160 132, 3 between 170 and 200	240-260 m ~316, 324 m (gen. dec. >300) ~290, 317 w 267, 286 s 300-340 m
AgNO ₃ KN ₃ + Ag NO ₃ (38 mol %) (19 mol %)	120, 168 125, 170 120, 167, 176	230-270 m 210, 285 w 313 vw
KN ₃ + Cd(NO ₃) ₂ (50 mol %) (25 mol %)		
(13 mol %) (8.8 mol %) (5.5 mol %)		
(14.2 mol %) (9.1 mol %) (5.1 mol %)		

^a All samples contained metallic calcium.^b Highest temperature is that of the melting endotherm; others are lattice transitions.^c Single temperature is that of peak of exotherm; s = strong, m = moderate, w = weak, and v = very.

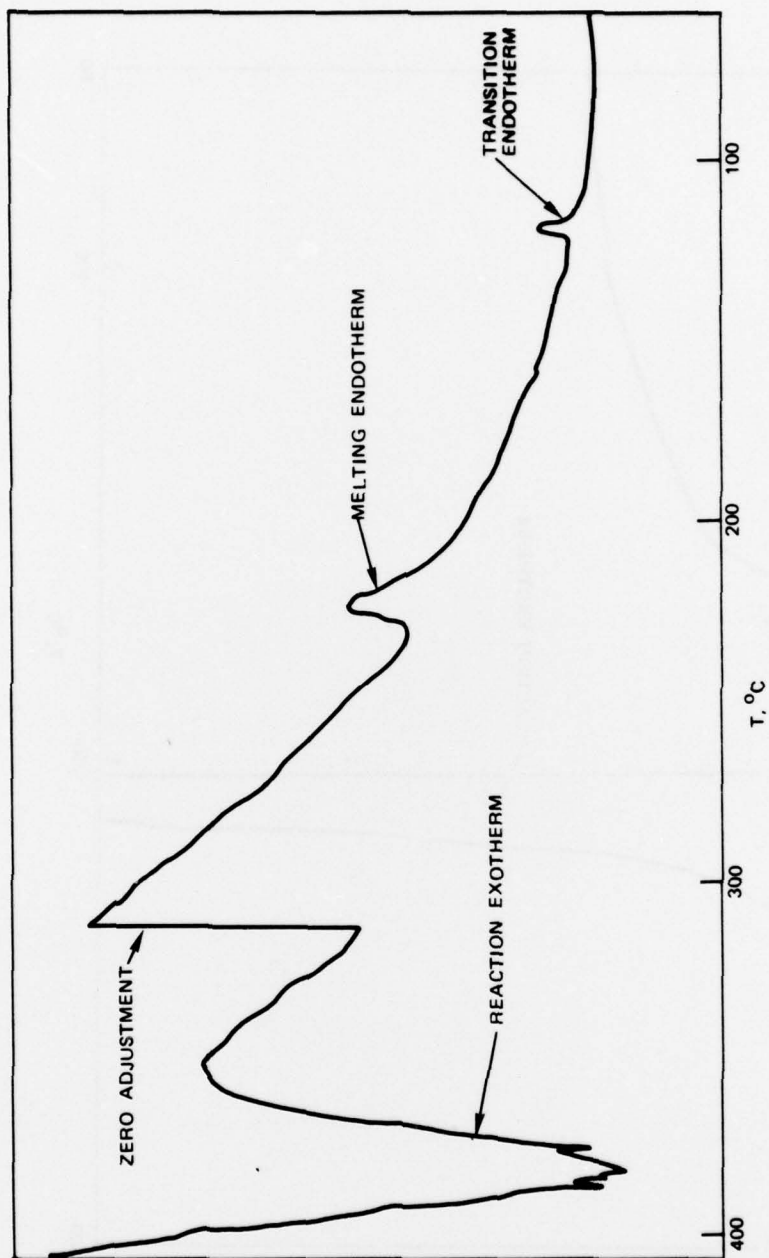


FIGURE 4. DSC Trace of Calcium in $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3 + \text{CuCl}$ (6.7 mol %).

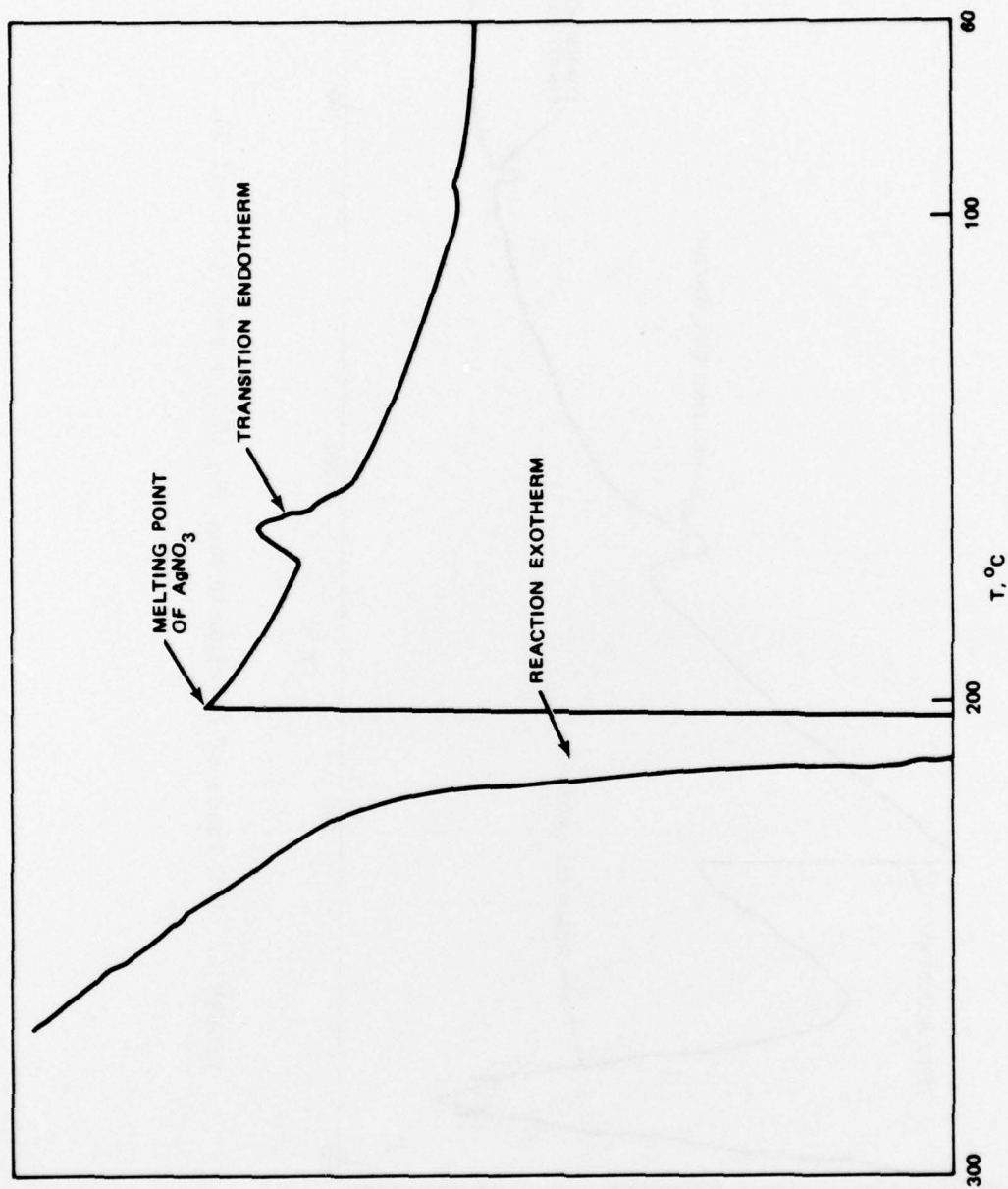


FIGURE 5. DSC Trace of Calcium in AgNO_3 .

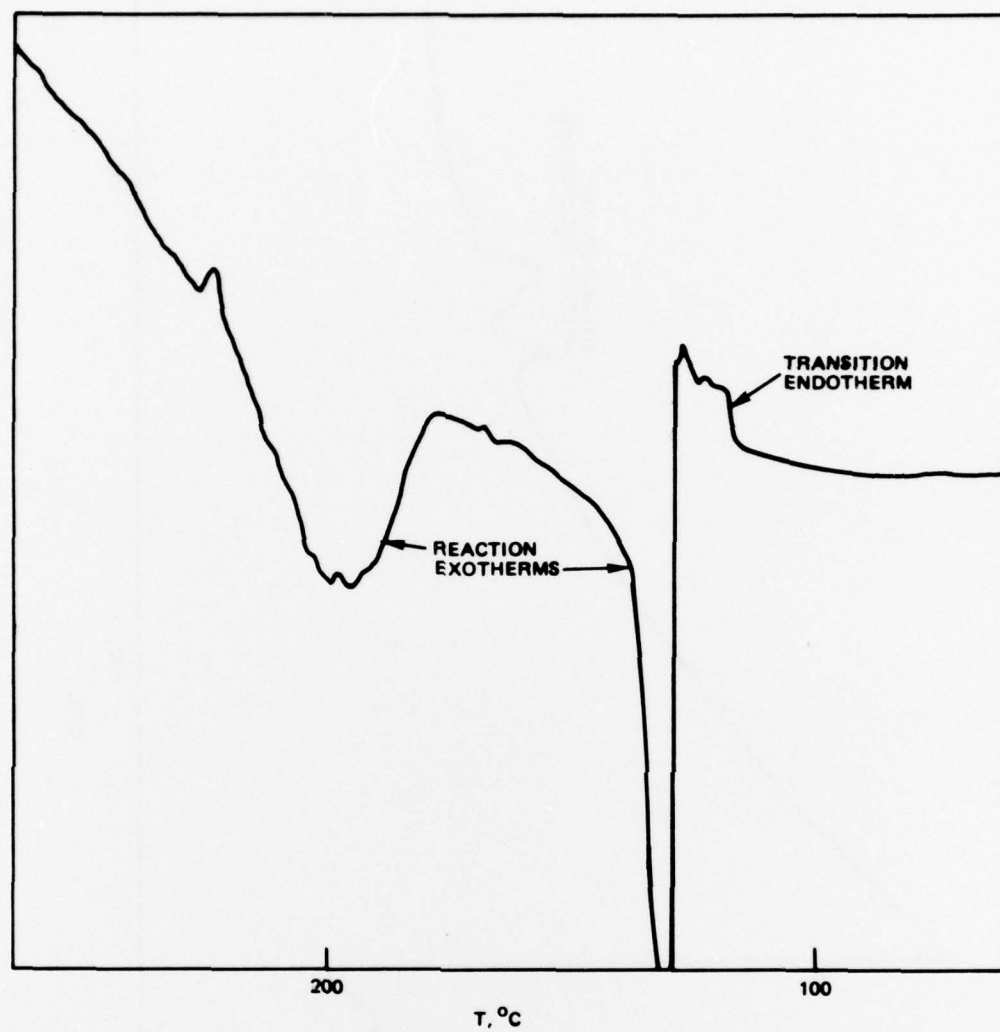


FIGURE 6. DSC Trace of Calcium in $\text{KNO}_3 + \text{AgNO}_3$ (38 mol %).

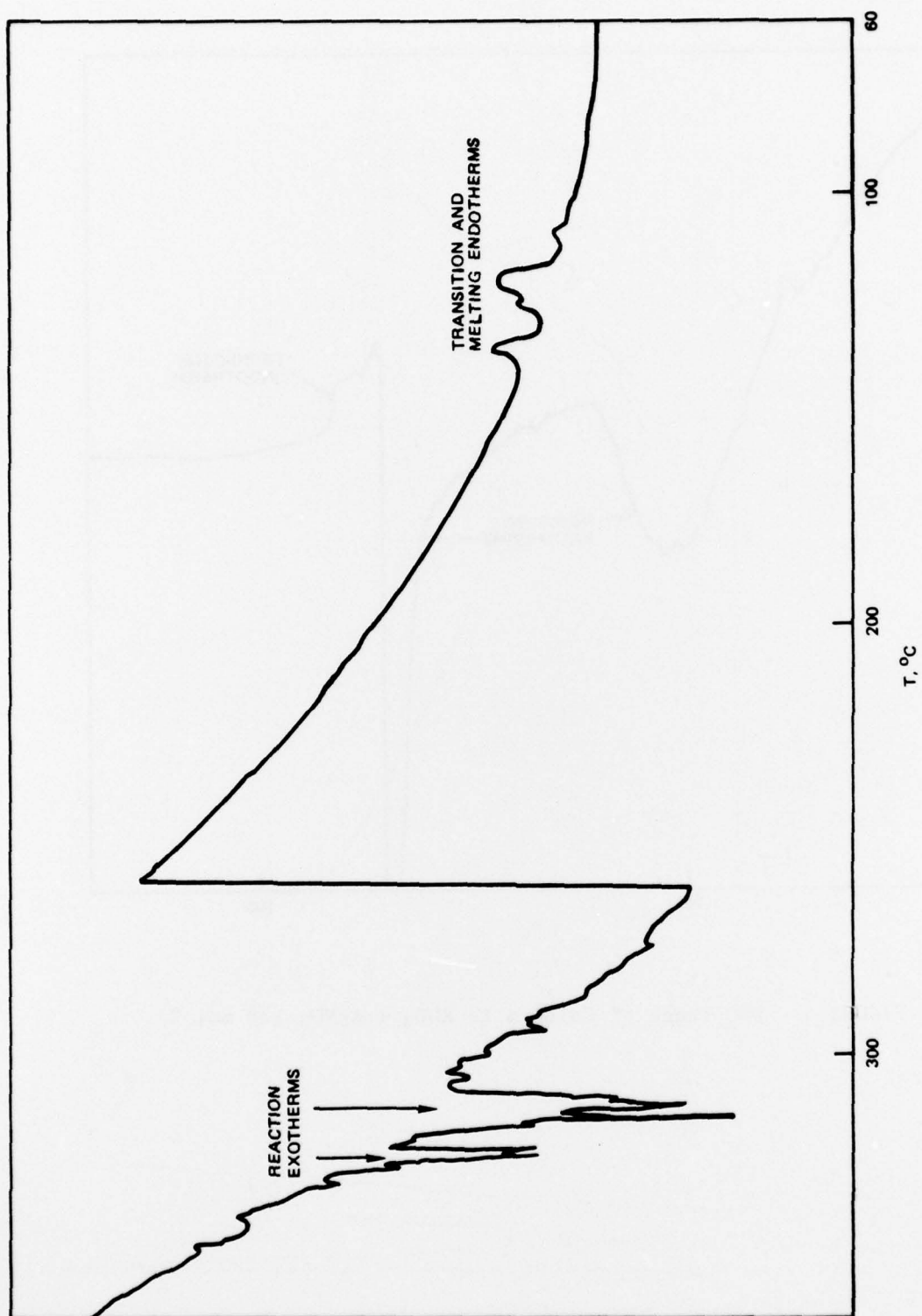
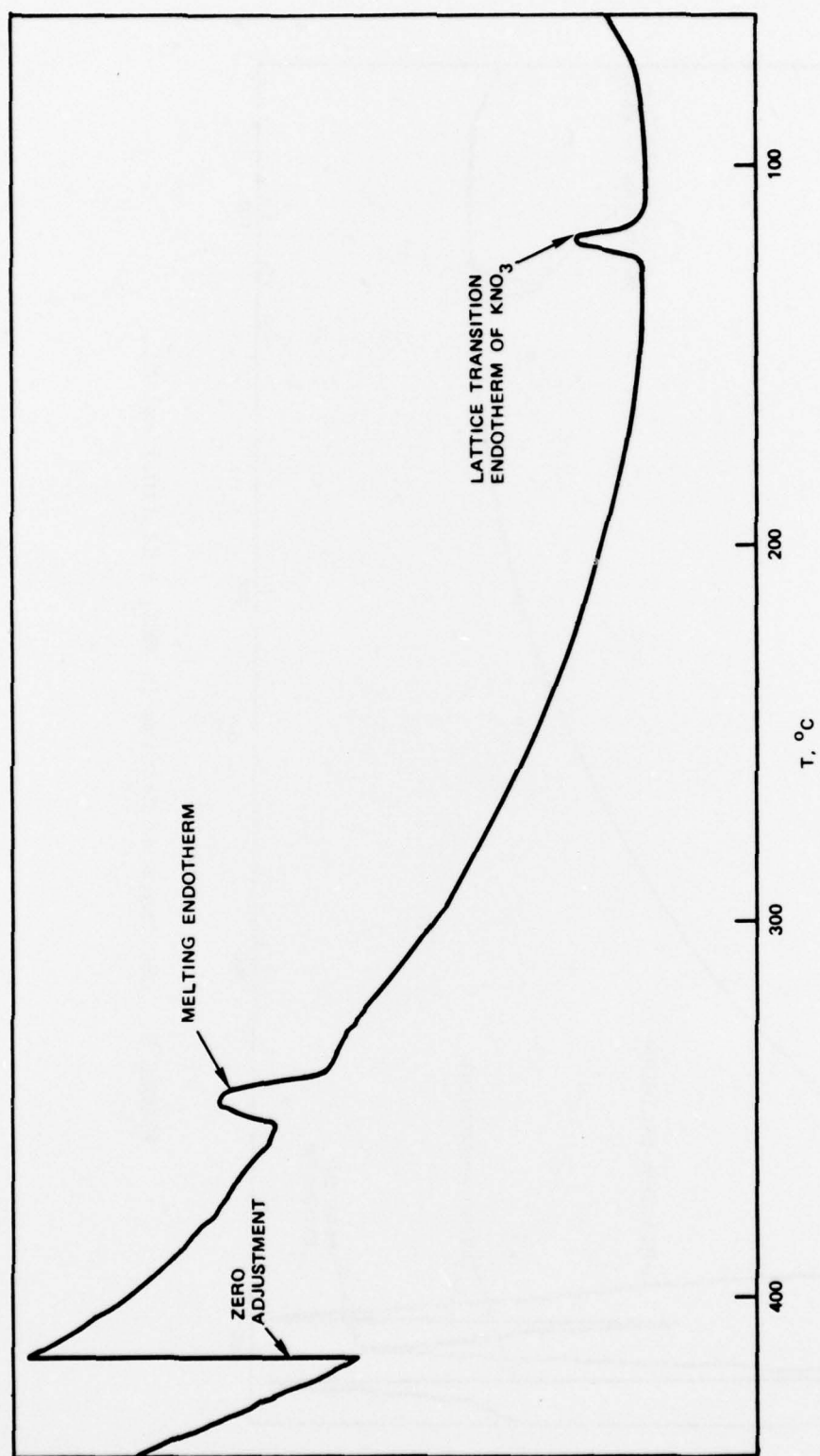


FIGURE 7. DSC Trace of Calcium in $\text{KNO}_3 + \text{AgNO}_3$ (8.8 mol %).

FIGURE 8. DSC Trace of $\text{KNO}_3 + \text{KI}$ (10.1 mol %).

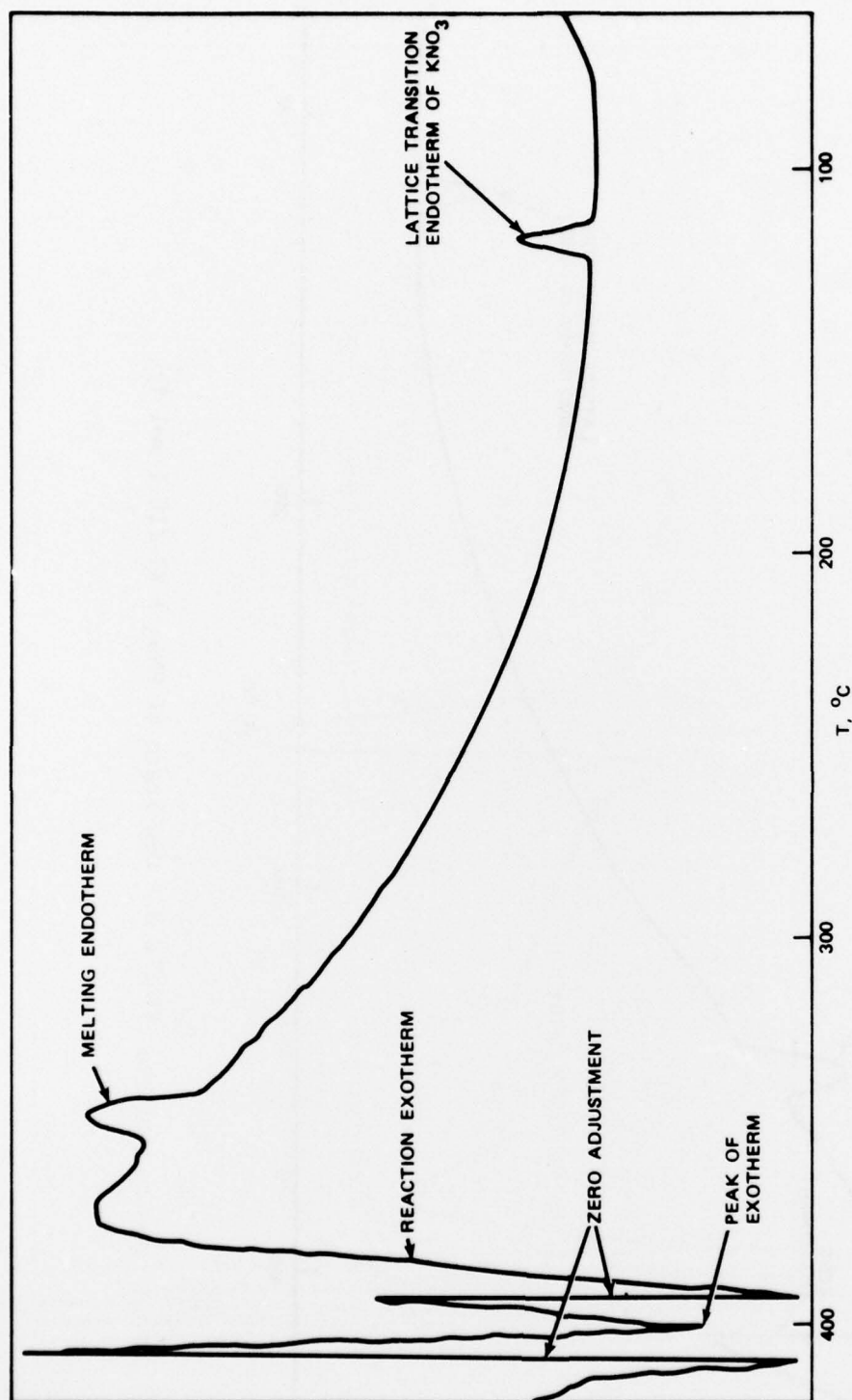


FIGURE 9. DSC Trace of Calcium in KNO_3 + KI (10.1 mol %).

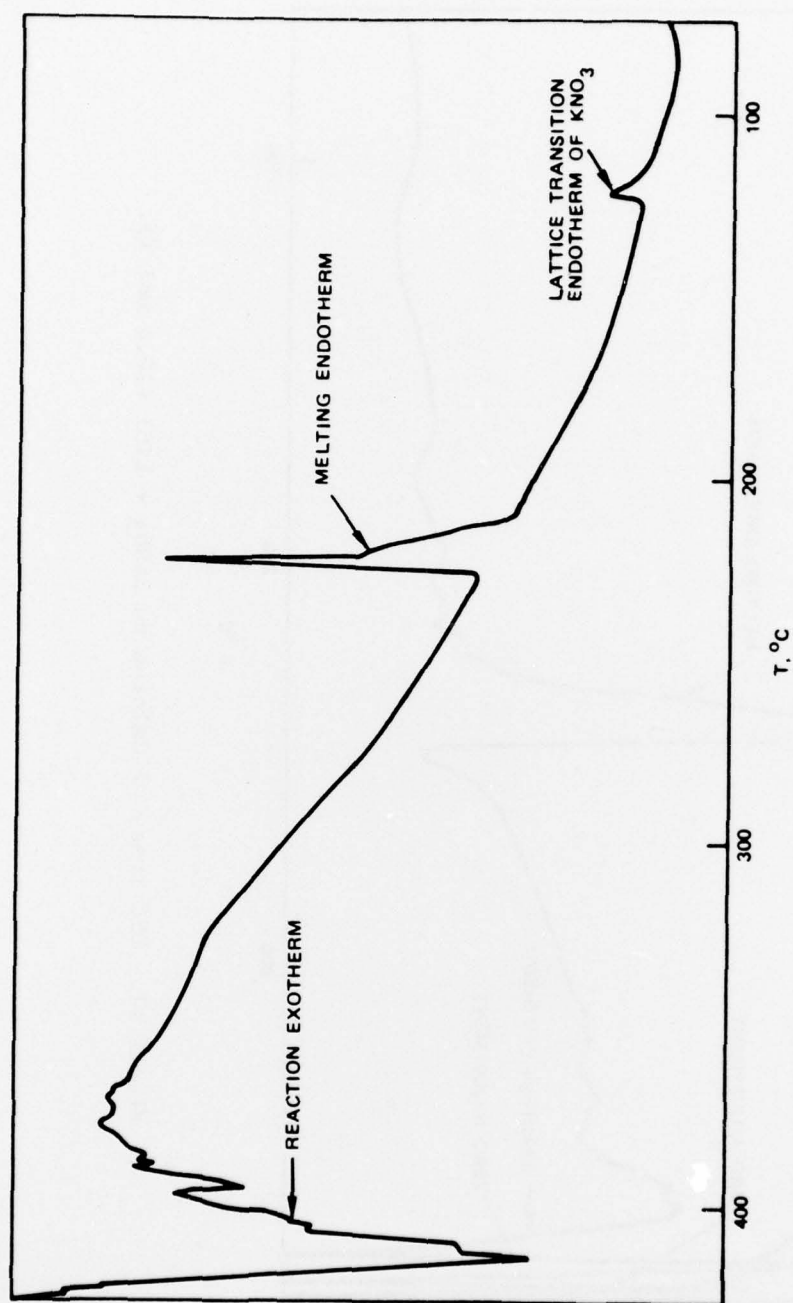


FIGURE 10. DSC Trace of Calcium in $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3 + \text{KBr}$ (8.0 mol %).

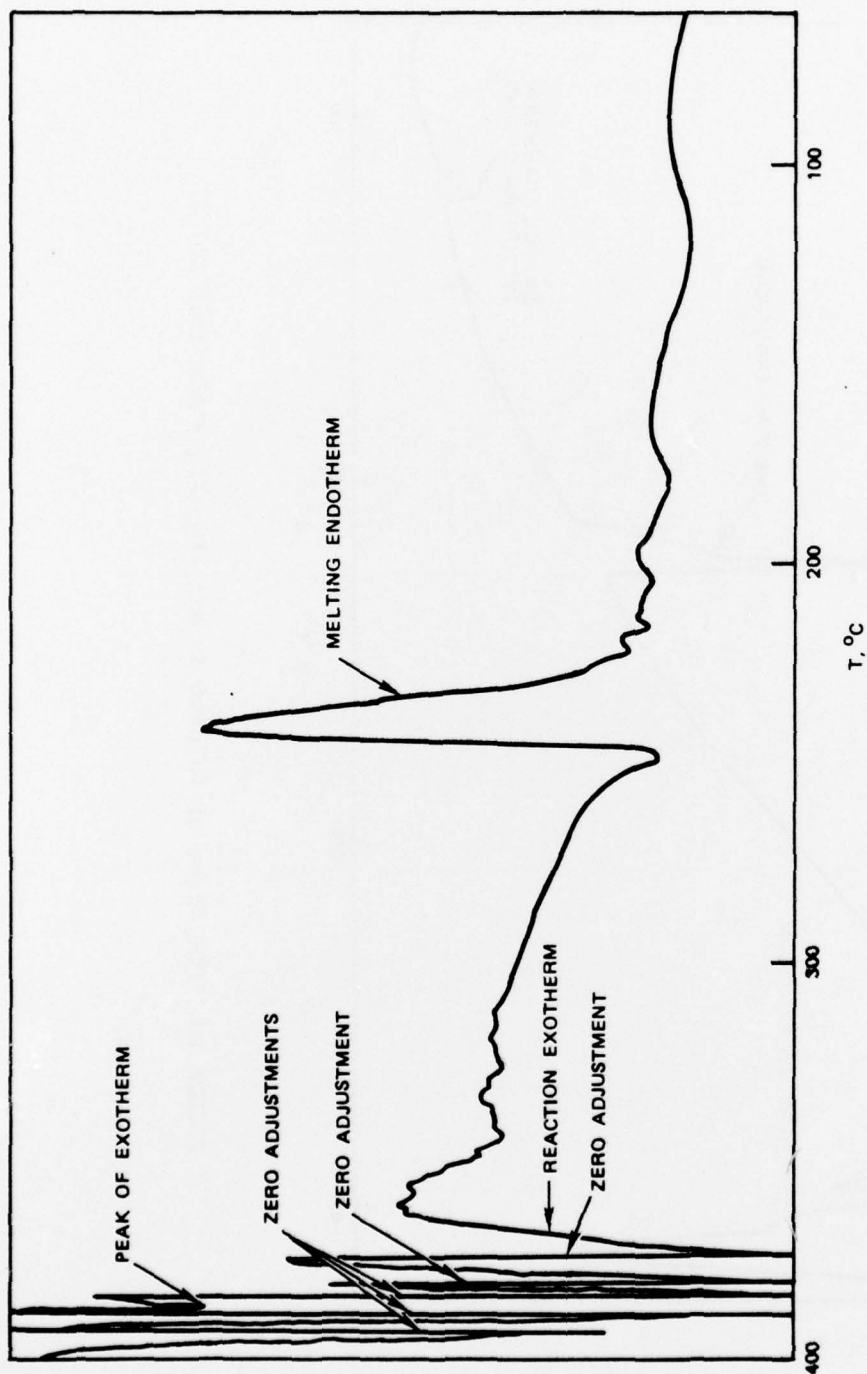


FIGURE 11. DSC Trace of Calcium in $\text{LiNO}_3 + \text{LiCl}$ (10.6 mol %).

TABLE 3. DSC Results for Calcium in Mixtures of Nitrates and Halides.

Nitrate	Halide	Mol % Halide	Endotherms, °C ^a	Exotherms, °C ^b
LiNO ₃	LiCl	12.5	240	>320 vs; flashes, sample flips out of holder
		11.0	240	>320 vs; same behavior as 12.5%
		10.6	240	>320 s; off scale, but no flashing
		10.1	240	Dec. >330
		10.0	230	372 m
		4.9	230	Dec. >380; no strong exos.
		10.2	115, 125, 240	None
		10.2	164, 240	None
		10.2	220	365 s
		10.3	240	340 s
NaNO ₃	KF	10.0	305	395 m
	KF	10.8	290	400 m
	CaF ₂	9.9	310	414 w
	KCl	10.3	218, 282	415 m
	CaCl ₂	10.3	280	350 s
	NaBr	10.2	300	395 m
	KBr	10.2	220, 285	405 s
	NaI	10.0	300	345 s
	KI	10.2	280	345 s
		10.9, no Ca	114, 310	None
KNO ₃	KF	10.9	118, 315	370 s
	KCl	12.3	120, 335	~400 w
		10.5	120, 330	None
	LiCl	5.0	115, 320	360 w, 415 s
	KBr	10.3	116, 340	None
	KI	10.1, no Ca	120, 345	None
		9.2	120, 345	386 s

See footnotes at end of table.

TABLE 3. (Contd.)

Nitrate	Halide	Mol % Halide	Endotherms, °C ^a	Exotherms, °C ^b
Na _{0.5} K _{0.5} NO ₃	KF	12.4	115, 120	390 m
		5.7	120, 225	386 m
	LiCl	10.5	114, 220	Series at >320; peak at 405
	KCl	12.7, no Ca	118, 220	None
		12.7	118, 220	385-390 m
		8.7	104, 115, 216-221	330, 395 m
		3.9	112, 217	408 m
		2.7	120, 222	410 w
		1.6	120, 220	420 w
		0.62	120, 220	None
RbNO ₃	NaBr	9.5	115, 214	398 s
	KBr	11.5	118, 215	410 s
		8.0	120, 220	414 m
		4.6	118, 220	395, 410 w
	KI	10.1	120, 230	Series at >320; peak ~400; s
		5.1	120, 230	375 m
	NaF	11.1	163, 235, 294, 317	368, 388 s
	KF	11.0	150, 160, 260	357 s
	CaF ₂	10.5	163, 235, 294, 320	None
	KCl ₂	20.0	160	375 w
		10.3	160, 325	None
	CaCl ₂	10.3	160, 210	355, 374 m
	KBr	10.3	160, 290	435 w
	KI	10.2	165, 295	394 m

^a Highest temperature is that of the melting endotherm; others are lattice transitions.

^b Temperature given is that of the highest peak of the exotherm. Most exotherms were broad and many had several peaks; s = strong, m = moderate, w = weak, and v = very.

10 and 11 mol % cause a strong exotherm but no flashing, and concentrations ≤ 5 mol % cause no perceptible reaction. The effect of solubility is seen in the runs with calcium fluoride and chloride--calcium fluoride produces little or no reaction, whereas the much more soluble calcium chloride produces a strong reaction.

CONCLUSIONS

The DSC studies reported here indicate that molten nitrates show promise for use as electrolytes in thermal batteries. They form a passivating layer on calcium which inhibits corrosion. The layer can be broken down in a controllable manner by the addition of certain Lux-Flood acids or halides, so as to increase the probability of electrochemical reaction of the calcium with nitrate or other oxidizers. The halides offer an especially convenient means of control. A separate study that addresses the problem of the electrochemical nature of the calcium electrolyte interface has been submitted for open literature publication.

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